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STABILIZATION OF THE SOLVENT METHYL-N-AMYL KETONE (MAK) 1/1
IN VINYL PAINTS(U) CONSTRUCTION ENGINEERING RESEARCH
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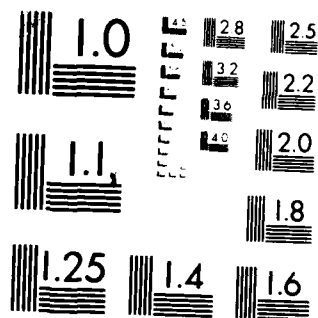
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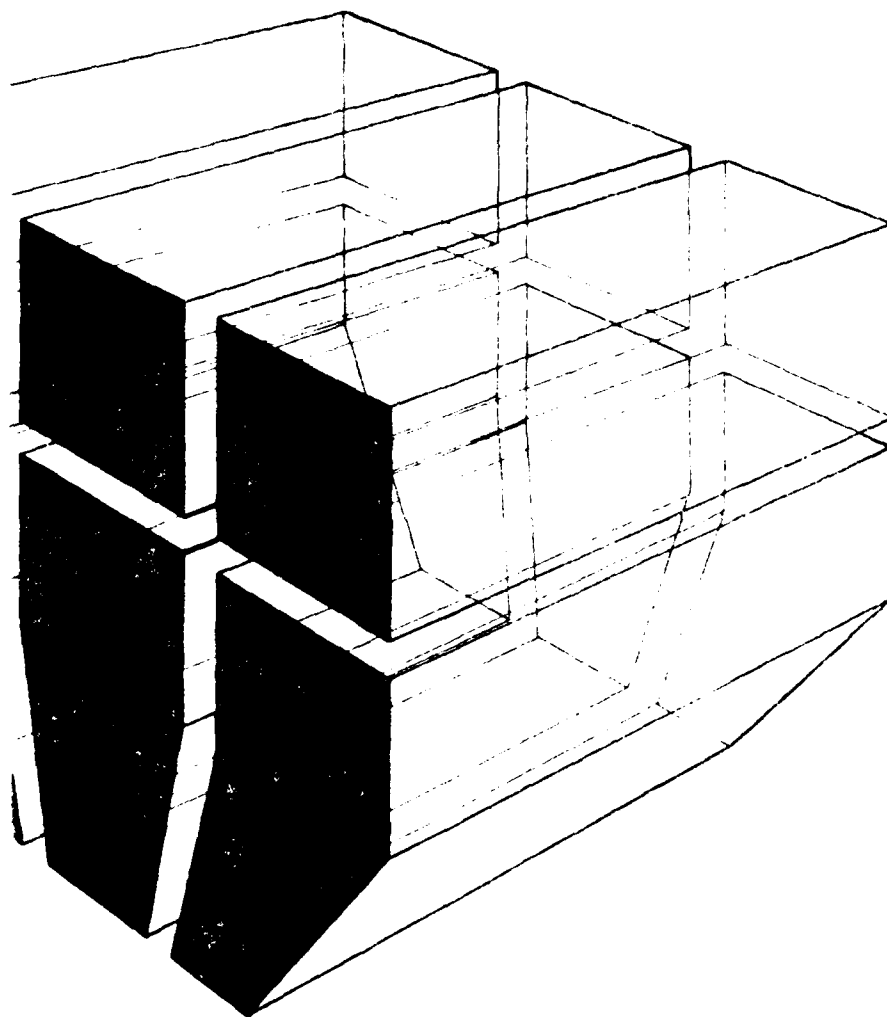


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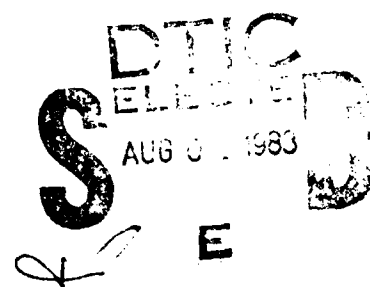
TECHNICAL REPORT M-331
June 1983
Development of High Performance Coatings

STABILIZATION OF THE SOLVENT
METHYL-N-AMYL KETONE (MAK)
IN VINYL PAINTS

AD A 131059



by
Armand F. Lange
Alfred D. Beitelman



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ERRATA SHEET

for

CERL Technical Report M-331, *"Stabilization of the Solvent Methyl-n-Ketone (MAK) in Vinyl Paints,"* June, 1983.

Throughout this report the chemical spelled 2,4,6-tris(dimethylaminoethyl) phenol should be spelled 2,4,6-tris(dimethylaminomethyl) phenol.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) — This research was conducted to devise a way to eliminate the formation of acids during storage of vinyl paint by controlling the acidity of its solvent— methyl-n-amyl ketone (MAK). MAK was found to break down under organic acid catalyzed conditions. The decomposition products, acetic and pentanoic acids, were formed by an oxidation reaction. The reaction is autocatalytic, since the products formed are the catalysts for further reaction. 2-ethyl hexanoic acid was found in the original MAK, but was not produced by the organic-acid-catalyzed oxidation. Under most chromatographic conditions, pentanoic acid would elute very close to MAK and therefore		

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→ would not be detected. The reaction products suggest that a peroxide is involved in the oxidation.

Inhibitors which would eliminate peroxide formation were tested as stabilizers for MAK. Ethanol was found to stabilize MAK to a limited extent. Other inhibitors tested which were successful were 2,2'-bis(4-hydroxyphenyl) butane, hydroquinone monobenzyl ether, and 2,4,6-tris(dimethylaminoethyl) phenol. These are all peroxide inhibitors. It is recommended that any of these inhibitors be used with ethanol in the final paint formulation. ←

FOREWORD

This research was conducted for the Directorate of Civil Works, Office of the Chief of Engineers (OCE), under Project CWIS 31205, "Development of High Performance Coatings." Mr. Robert Kinsel (DAEN-CWE-E) was the OCE Technical Monitor.

The work was conducted for the Engineering and Materials Division (EM) of the U.S. Army Construction Engineering Research Laboratory (CERL) by the University of Iowa Hygienic Laboratory, Oakdale Campus, Iowa City, IA, under Contract DACA 88-82-C-005. Mr. Alfred Beitelman is the CERL point of contact. Dr. R. Quattrone is Chief of CERL-EM.

COL Louis J. Circeo is Commander and Director of CERL, and Dr. L. R. Shaffer is Technical Director.

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STABILIZATION OF THE SOLVENT METHYL-N-AMYL KETONE (MAK) IN VINYL PAINTS

1 INTRODUCTION

Background

The U.S. Army Corps of Engineers uses special formulation vinyl paints to protect many of its locks and dams from corrosion. Although there are many special formulation paints, the most common is V-766 (see Appendix A). V-766 is available in two forms: V-766e for most routine painting, and V-766e(AP) for use where state or local air pollution control regulations control the use of paints containing photochemically reactive solvents. The chief solvent in the V-766e(AP) paint is a nitroparaffin solvent containing 2-nitropropane.

In 1980, the U.S. Department of Labor's Occupational Safety and Health Administration (OSHA) and the U.S. Department of Health and Human Services' National Institute for Occupational Safety and Health (NIOSH) published a joint Health Hazard Alert.¹ This alert stated that 2-nitropropane is a confirmed animal carcinogen and a potential human carcinogen. The Corps of Engineers' initial response was to inform all Division Engineers and laboratories of the problem and stress the need for the use of personal protection equipment and procedures and physical examinations. To solve the problem over the long term, the Corps requested that the U.S. Army Construction Engineering Research Laboratory (CERL) evaluate coatings for replacement of 2-nitropropane with a solvent that is nontoxic, environmentally safe, and meets performance standards.

CERL has conducted many background studies of vinyl paints. One recent study² reports CERL's evaluation of formulation No. 1253 (see Appendix B). This material was found to have excellent application, performance, and safety properties, but could

not be used because of the instability of the solvent methyl-n-amyl ketone (MAK). However, the need to replace the solvent 2-nitropropane caused renewed interest in formulation No. 1253.

Some preliminary investigations conducted by CERL and by Eastman Chemical, the manufacturer of MAK, revealed that the instability resulted when oxidation of the solvent produced an acidic condition. One of the acids identified was 2-ethyl hexanoic acid; however, its presence could not be explained through normally expected chemical reactions. Further work showed that peroxide inhibitors and reactive chain inhibitors appeared to be effective forms of stabilization, but were not completely successful. It was therefore decided to conduct an in-depth study of the acidity of the solvent MAK.

Objective

The purpose of this study is to devise a way to eliminate the formation of acids during storage of vinyl paint by controlling the acidity of MAK, either by adding a stabilizing agent or by changing the manufacturing process.

Approach

First, the mechanism of MAK breakdown and acid formation had to be ascertained; then, based on the mechanism discovered, a method of controlling or eliminating the acid formation would be determined. As one practical chemical means of control, stabilizers chosen on the basis of the MAK breakdown mechanism would be evaluated for effectiveness and for compatibility with the paint formulation.

The first step in solving this problem was to identify the impurities in commercial MAK. Next, purified MAK, prepared by distilling commercial MAK, was reacted under various conditions. Deuterated MAK was then used to confirm the proposed mechanism of the reaction which produced the acid. This information was then used to choose inhibitors of acid formation. These inhibitors were tested under conditions that produced the impurities normally found in acidic MAK. The best of these inhibitors were then tested in paint formulations for acid formation and for adhesion and tendency to blister.

Mode of Technology Transfer

It is recommended that formulations developed by this study be incorporated into Civil Works Guide Specification CW 09940, *Painting: Hydraulic Structures and Appurtenant Works*.

¹Health Hazard Alert, Publication No. 80-142 (Occupational Safety and Health Administration and the National Institute for Occupational Safety and Health, 1980).

²A. Beitelman and R. Lampo, *Preliminary Selection of Compatible Solvents for Vinyl Paints*, Special Report M-261 ADA067708 (U.S. Army Construction Engineering Research Laboratory, 1979).

2 PROCEDURE

Identification of Impurities in MAK

The impurities in commercial MAK were extracted with acid, basic, and neutral solutions. The impurities tested for included water, esters, organic acids, and organic bases. The extracts were neutralized and analyzed, primarily by gas chromatography/mass spectrometry (GC/MS). Selective extraction and concentration allowed identification of the trace (100 ppm and less) organic materials present.

Reaction of Purified MAK

A large batch of commercial MAK was purified by means of a spinning-band distillation apparatus. Using GC/MS analysis, the product was found to be greater than 99.9 percent pure (see Figure 1). The purified MAK was then reacted under acid, basic, neutral, and metal-catalyzed conditions. The intention of this step was to duplicate, in a laboratory setting, the formation of impurities found in commercial MAK. The catalysts used were:

1. Acid catalyst—0.100 mL 1 Normal H_2SO_4 in ethanol
2. Basic catalyst—0.100 mL 1 Normal KOH in ethanol
3. Neutral—nothing added
4. Metal catalyst—100 mg metal from storage can (Fe).

The reaction conditions for the acidic, basic, and metallic catalysts were: 10 mL MAK purified by distillation, 0.10 mL 1 normal catalyst or 100 mg metal, and 0.100 mL water (if used). These catalysts were each added to the MAK under the following three sealed conditions: dry air, dry air plus 0.100 mL water, and dry nitrogen. To speed the reaction, the samples were sealed in 25-mL glass ampules and reacted at 60°C for 100 hours. The samples were cooled to below room temperature, opened, and then analyzed by GC/MS.

A second set of reactions was set up using MAK with a high acid number as a catalyst. Purified MAK was catalyzed with 0.01 percent high acid number MAK and refluxed for 16 hours. The reaction was repeated with the addition of a trace (0.1 percent) of water. These reactions were repeated, using the

conditions outlined in the previous section for reaction of purified MAK. The reaction products were analyzed by GC/MS.

The purified MAK was then reacted with the following organic acid catalysts: acetic acid, butyric acid, formic acid, hexanoic acid, 2-hexanoic acid, high acid number MAK, and pot residue from distillation of MAK. The reactions were run as before, except that oxygen was used instead of air. The reaction conditions were: 5 mL MAK purified by distillation and 0.010 mL catalyst ("Bad"* MAK, organic acid). The reactants were sealed in a 125-mL flask after being flushed with "chemical purity" oxygen and held at 60°C for 100 hours. The reaction products were analyzed by GC/MS.

Reaction of Deuterated MAK

The deuterated MAK was reacted, using "Bad" MAK as a catalyst, and employing the same procedures used for the purified MAK. Deuterated MAK (d_5 1,1,1,3,3-2-heptanone), was obtained which would be specific for reaction at either side of the ketone group. The deuterated MAK was reacted under conditions that produced the impurities found in commercial MAK. The reaction products were analyzed by GC/MS. The reaction conditions were: 1 mL MAK and 0.010 mL of catalyst. The reactants were sealed in a 125 mL flask being flushed with "chemical purity" oxygen and held at 60°C for 100 hours.

Determination of Inhibitor Effects

Distilled MAK was reacted with "Bad" MAK as a catalyst in the presence of various inhibitors. The reaction conditions were 1 mL distilled MAK, 0.1 mL "Bad" MAK, and 100 ppm of inhibitor.

The reactants were placed in a 120-mL vial which was flushed with oxygen, sealed, and placed in a 60°C water bath. Duplicate samples were run, and the reaction was terminated at 100 and 500 hours by freezing the samples. The samples were analyzed by gas chromatography and the results confirmed by GC/MS.

Ethanol was chosen as one of the inhibitors to see if the production of peracid could be stopped. Ethanol is normally used as an oxidation inhibitor in ethers to prevent peroxide formation. The level of ethanol

*High acid MAK.

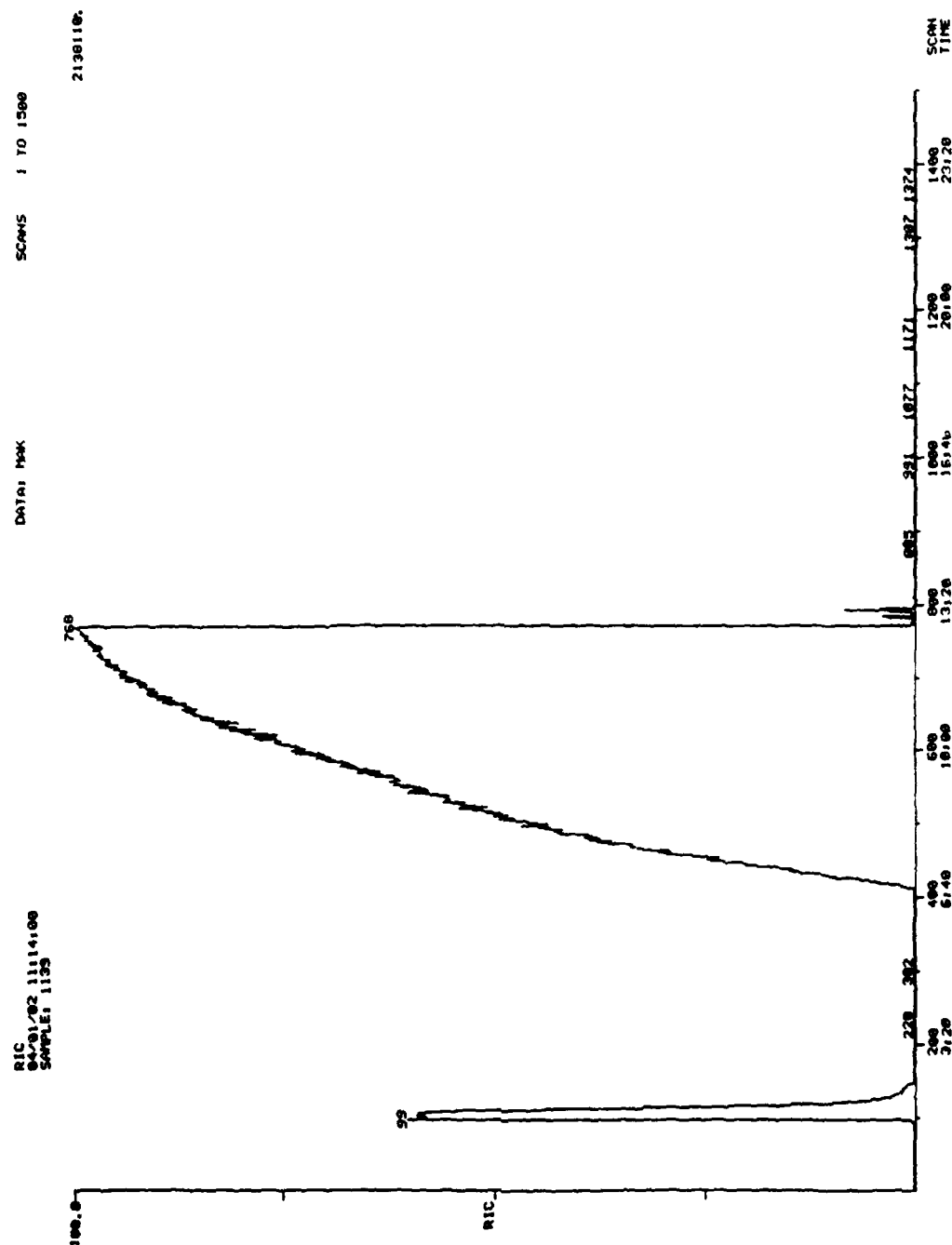


Figure 1. Reconstructed ion chromatogram (RIC) of purified MAK.

used was 2 percent of the MAK. The reaction conditions were the same as used for the other inhibitors.

Testing Effects of Inhibitors on Paints

To determine any adverse effects of the inhibitors, paints were made up according to formulation No. 1253 (see Appendix B). The following levels of inhibitor were added to samples of the paint formulation:

1. Ethanol—2 percent on MAK.
2. Hydroquinone monobenzyl ether—100 ppm on paint.
3. 2,2'-Bis(4-hydroxyphenyl) butane—100 ppm on paint.
4. 2,4,6-Tris(dimethylaminoethyl) phenol—100 ppm on paint.

The paint formulations were applied to a 3- x 5-in. sheet of steel to test for adhesion and for blistering in water. In addition, a 2-mL sample of each formulation was placed in a 125-mL vial, flushed with oxygen, sealed, and aged by placing in a 60°C water bath for 300 hours. These paints were then analyzed for acetic and pentanoic acids by GC and GC/MS.

GC/MS Analysis Conditions

The following conditions were used to analyze the reaction mixtures:

Chromatographic Conditions

0.25-mm x 30-m fused silica capillary column, helium flow of 25 cc/second

50°C initial temperature for 4 minutes, then 8°C per minute up to 210°C and held for 20 minutes.

Mass Spectrographic Conditions

Electron multiplier, 1905.888 V; electron energy, 70 eV; emission current, 0.5 mA; ion energy 9.02 V.

3 RESULTS AND DISCUSSION

Identification of Impurities

The initial GC/MS analysis of the impurities in

Table 1
Chromatogram Results

Attached RIC Scan Number (From Figure 2)	Compound
26	Formic acid
130	Formic acid, methyl ester
231	Propanol
414	2-ethyl hexanol
494	Methyl furan
738	2-hexanone
778	Acetic acid
791	Pentanoic acid
971	2-heptanone (MAK)
1083	2-ethyl hexanoic acid

commercial MAK showed that several compounds were present. The reconstructed GC/MS ion chromatogram (RIC) is shown in Figure 2, and each compound's position in the chromatogram is given in Table 1.

Reaction of Purified MAK

The formic, acetic, and pentanoic acids could be the reaction products of oxidation. The other compounds could be the results of a rearrangement reaction. The alcohols and the 2-ethyl hexanoic acid could indicate that either a Claisen condensation reaction or a Cannizzaro reaction occurred. To test this hypothesis, a series of reactions was set up in which the purified MAK was first catalyzed and then uncatalyzed.

Purified MAK was reacted under acidic, basic, neutral, and metal-catalyzed conditions. There was either essentially no reaction or no reaction that led to the formation of organic acids; however, condensation products, such as methyl furans and methyl pyrans, were formed. The presence of moisture in two sets of reactions reduced the production of condensation products. There was no detectable 2-ethyl hexanoic acid or aldehyde at the method detection limit of 10 ppm. When the experiments were repeated, the results were the same. The original assumptions of a Claisen condensation or Cannizzaro reaction were therefore disproved.

In an attempt to duplicate the formation of acids in MAK, "Bad" MAK was used as a catalyst in a preliminary experiment. Purified MAK was catalyzed with 0.01 percent "Bad" MAK and refluxed for 16 hours. Analysis of the MAK after reaction showed the presence of formic, acetic, and hexanoic acids. Although pentanoic acid was found to co-elute with the MAK under the chromatographic conditions

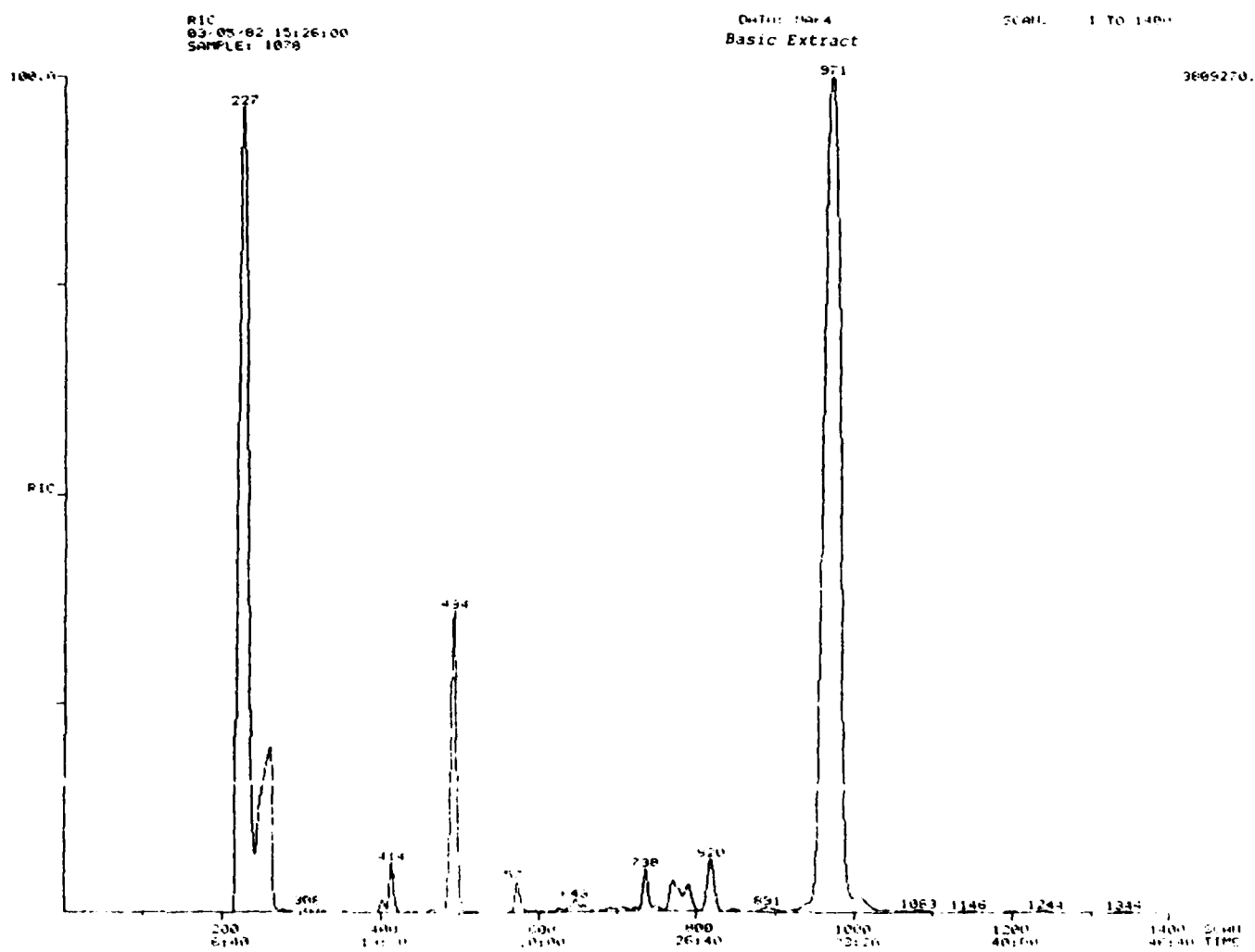


Figure 2. RIC of basic extraction of MAK.

used, it could still be detected by the use of ion monitoring on the GC MS (see Table 2). When purified MAK was refluxed for 16 hours with "Bad" MAK plus a trace of water, even fewer organic acids were produced. Analysis of purified MAK refluxed for 16 hours without a catalyst showed that no acids were produced.

When these procedures were repeated under the controlled conditions used in the previous degradation experiments, they yielded the same organic acids previously produced.

To increase the speed with which organic acids formed in these experimental reactions, the reaction vials were filled with oxygen instead of air. The reaction using "Bad" MAK as a catalyst was repeated, and organic acids were detected in the final reaction mixture. The reactions were repeated, using "Bad" MAK, acetic acid, butyric acid, formic acid, hexanoic acid, 2-hexanoic acid, and pot residue from the distillation of MAK, respectively, as catalysts. Purified MAK without a catalyst was also run as a control.

There was almost no acid formation when formic acid was used as a catalyst. When no acid catalyst was used, the control reaction produced no acids; however, organic acids were found when acetic acid, butyric acid, hexanoic acid, 2-hexanoic acid, "Bad" MAK, and pot residue were used as catalysts.

Acetic and pentanoic acids comprised the majority of acids produced in these reactions. Formic acid and hexanoic acid were present, but at a much lower level.

No products were formed that could be derived from 2-ethyl hexanoic acid or aldehyde, nor were any compounds detected that could be considered precursors of these compounds. These results indicate that the 2-ethyl-hexyl derivatives were already present in the commercial MAK. These unusual materials would be easily detected and would tend to obscure the formation of other less easily detected acids (e.g., pentanoic). There was no indication of a Claisen condensation reaction taking place, since no high molecular weight compounds were present. There was also no evidence of a Cannizzaro reaction, since none of the alcohols that it should produce were found.

The results of these reactions indicate that the acid formation is an oxidation reaction catalyzed by the organic acids found in the commercial MAK. The reaction is auto-catalytic, since the products formed are the catalysts for further reaction. That this reaction is catalyzed by organic acids in general, and not specifically those detected in the MAK, was demonstrated by the ability of butyric acid and 2-hexanoic acid to catalyze the breakdown of MAK to organic acids.

Reaction of Deuterated MAK

When reacted with "Bad" MAK as a catalyst, the deuterated MAK produced deuterated acetic acid (see Figure 3) and nondeuterated pentanoic acid (see Figure 4). This would confirm an oxidation reaction that takes place with loss of the hydrogens alpha to the carbonyl group on the 3-position of 2-heptanone. Therefore, a change to a ketone solvent that does not have alpha hydrogens would reduce acid formation.

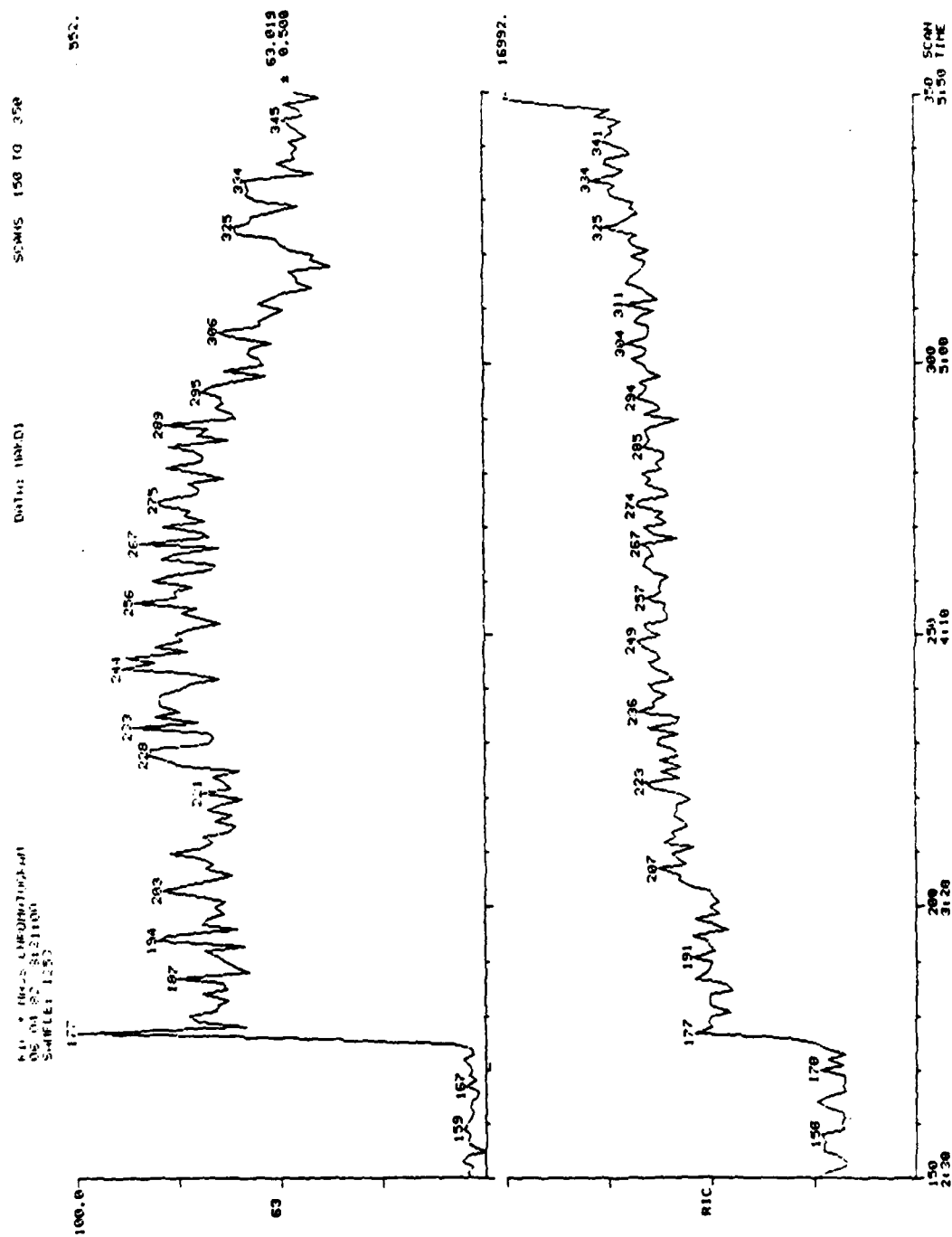
Table 2
Products of Reaction

Catalyst	Acids Detected*			
	Formic Acid	Acetic Acid	Pentanoic Acid	Hexanoic Acid
High Acid MAK	1	P	P	1
Acetic Acid	1	P	P	1
Butyric Acid	1	P	P	1
Formic Acid	P	1	1	1
Hexanoic Acid	1	P	P	1
2-Hexanoic Acid	1	P	P	1
Pot Residue	P	P	P	P

P Present

1 Trace

*No 2-ethylhexyl products were detected.



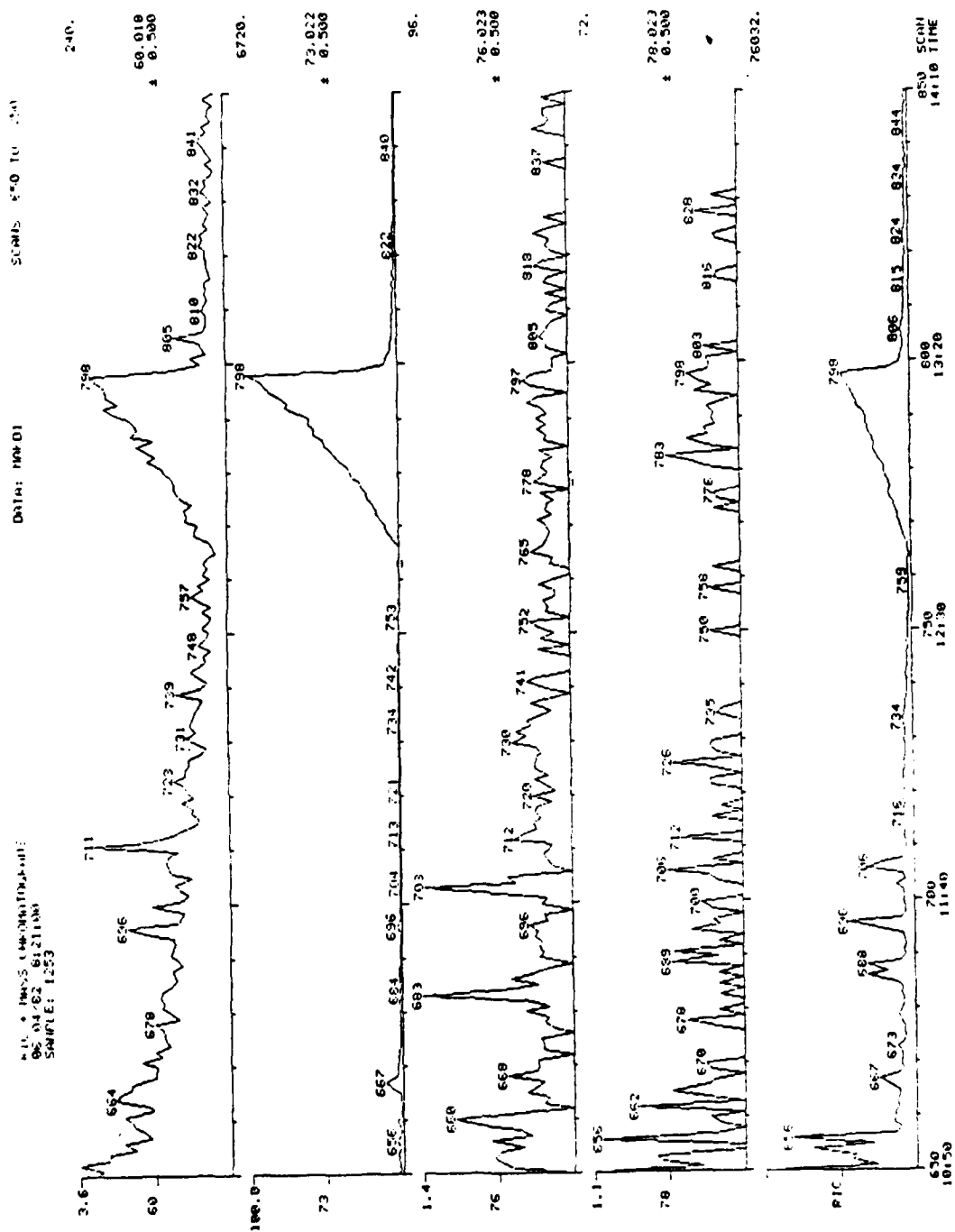


Figure 4. RIC and multiple mass chromatograms of MAK.

Mechanism of Acid Formation

Figure 5 shows the mechanism of acid formation via organic acid catalyses. This shows oxidation of the organic acids to the peracid, which then oxidizes the methyl ketone to diketone, which further breaks down into pentanoic and acetic acids. Although no diketone was detected in the final reaction mixture, this reaction is consistent with the following evidence:

1. No organic acids are formed in MAK without an organic acid being present as a catalyst.
2. The reaction is not catalyzed by inorganic acids.
3. With organic acids present, there are no break-down products detected which would indicate a reaction at other than the ketone group and at the carbon with hydrogens alpha to the ketone.
4. Reaction of d₅1,1,1,3,3-2-heptanone produces pentanoic acid and d₅1,1,1-acetic acid. No deuterated pentanoic acid was produced.
5. The reaction products are predominantly pentanoic and acetic acids, not hexanoic and formic acids.
6. The addition of water, which would reduce the presence of peracids, decreases the formation of organic acids.

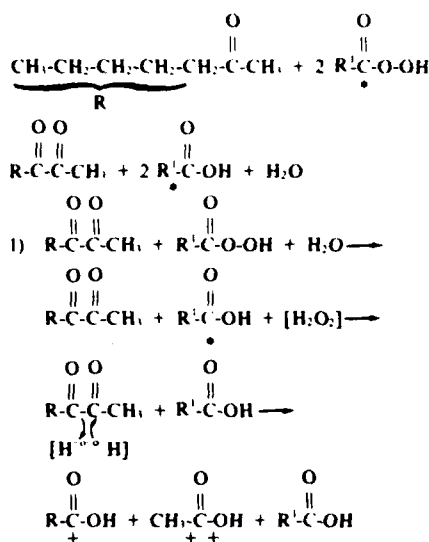
Results of Inhibitors Testing

Tables 3 and 4 list the inhibitors which were tested. From the initial acid formation at 100 hours, and the rate of acid formation from 100 to 500 hours, the three best inhibitors were found to be:

1. Hydroquinone monobenzyl ether
2. 2,2'-Bis(4-hydroxyphenyl) butane
3. 2,4,6-Tris(dimethylaminoethyl) phenol.

These inhibitors are the best when the results of formation and reaction rate studies of acetic and pentanoic acid are compared. No inhibitor will eliminate acid formation indefinitely; use of a good inhibitor with a low acid number MAK should significantly lower the acid formation level. Other inhibitors which appear to be good in one system only are:

1. Hydroquinone monomethyl ether



and/or

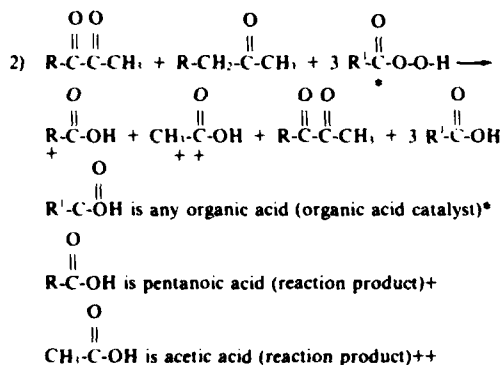


Figure 5. Mechanism of acid formation.

2. Dimethylaminoethyl phenol
3. N-phenyl-2-naphthylamine

All of these compounds appear to be radical inhibitors. This indicates that a free radical intermediate may be involved in the acid formation reaction.

When ethanol was tested as an inhibitor, the results (see Table 5) indicated that:

1. Without a catalyst, there is an induction period before the reaction of acid formation occurs.
2. The rate of acid formation starts out slow but increases with time.

Table 3
Inhibitors, Acetic Acid Results

Inhibitor	Acetic Acid Formed After Reaction for*		Reaction Rate**
	100 hrs	500 hrs	
2,2-Bis(4-hydroxyphenyl)butane	.26	.245	0
2,5-Di(1-amy)hydroquinone	.275	1.25	.24
Hydroquinone monobenzyl ether	.23	.245	.004
Hydroquinone monomethyl ether	.23	.245	.004
4-Methoxy-2,6-di-t-butylphenol	.27	.86	.15
Thiobis-(di-sec-amy)phenol)	.28	.86	.15
4,4'-Thiobis-(2-t-butyl-o-methylphenol)	.315	1.38	.27
Thiobisphenol	.32	1.61	.32
2,6-t-Di-butyl-a-dimethylamino-p-cresol	.24	1.09	.21
Dimethylaminomethylphenol	.25	.26	.003
2,4,6-Tris(dimethylaminoethyl)phenol	.25	.50	.06
6-Tert-butyl-m-cresol and sulfur dichloride rxn. product	.32	1.59	.32
N-phenyl-2-naphthylamine	.25	.25	0
Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	.27	.89	.16
Dilaurylthiodipropionate	.40	2.06	.42
Epoxidized soybean oil	.32	2.32	.50
2-Mercaptobenzothiazole	.51	6.2	1.42
2,4-Dihydroxybenzophenone	.32	2.3	.50
Hexamethylphosphoric triamide	.29	1.38	.27
BHT (2,6-ditert-butyl-4-methylphenol)	.24	1.84	.40
Tert-butyl hydroquinone	.36	1.17	.20
	.30	2.12	
No inhibitor	.28	2.23	.47
	ND	.97	
No inhibitor + no "Bad" MAK	.12	1.15	.25

*mg. mL.

** $\frac{\text{Acid Formed from 100 to 500 hours}}{400 \text{ hours}} \times 100 = \text{mg} \frac{\text{Acid Formed (mg, 100 hours)}}{100 \text{ hours}}$

ND - Not Detected (<0.05)

3. After 500 hours, there is still less acid than in the control.

4. The reaction rate is slower when ethanol is present.

In this series of reactions, another batch of purified MAK was used that assayed at 99.8 percent MAK by GC/MS. This could account for the differences in reaction rates between the inhibitor and the ethanol studies. After reaction, the MAK contained a large quantity of esters.

Results of Paint Analysis

The paints were made, applied to steel, and air-dried for 24 hours. The films formed on the steel were very good. The painted steel was placed in water for 72 hours, removed, and examined. No blistering or

nonadhesion was noted, so it was concluded that the inhibitors are not deleterious to the paint.

The painted steel coupons were scored diagonally, replaced in water for 3 weeks, and examined again. Oxidation had occurred where they were scored, but no blistering or nonadhesion was noted on any of the painted areas.

Analysis of the aged paint sample for acetic and pentanoic acids by GC/MS (see Table 6) showed that:

1. Although distilled MAK was used, there was still acid formation.

2. The inhibitors significantly reduced the amount of acid formed.

Table 4
Inhibitors, Pentanoic Acid Results

Inhibitor	Pentanoic Acid Formed After Reaction*		Reaction Rate**
	100 hrs	500 hrs	
2,2-Bis(4-hydroxyphenyl)butane	.18	.33	.038
2,5-Di(t-amyl)hydroquinone	.21	1.28	.27
Hydroquinone monobenzyl ether	.18	.31	.033
Hydroquinone monomethyl ether	.19	.40	.053
4-Methoxy-2,6-di-t-butylphenol	.21	.68	.12
Thiobis(di-sec-amylphenol)	.26	1.16	.23
4,4'-Thiobis(2-t-butyl-o-methylphenol)	.20	1.83	.41
Thiobisphenol	.24	1.63	.35
2,6-t-Di-butyl-a-dimethylamino-p-cresol	.36	1.36	.25
Dimethylaminomethylphenol	.25	.47	.055
2,4,6-Tris(dimethylaminoethyl)phenol	.25	.35	.025
6-Tert-butyl-m-cresol and sulfur dichloride rxn. product	.26	1.68	.36
N-phenyl-2-naphthylamine	.27	.46	.048
Polymerized 1,2-dihydro-2,2,4-trimethylquinoline	.22	.76	.14
Dilaurylthiodipropionate	.43	2.45	.51
Epoxidized soybean oil	.27	2.77	.63
2-Mercaptobenzothiazole	.52	6.55	1.51
2,4-Dihydroxybenzophenone	.27	2.48	.55
Hexamethylphosphoric triamide	.21	1.26	.26
BHT (2,6-di-tert-butyl-4-methylphenol)	.20	2.24	.51
Tert-butyl hydroquinone	.40	1.46	.27
	.32	2.22	
No inhibitor	.20	2.48	.52
	ND	.69	
No inhibitor + no "Bad" MAK	ND	1.40	.26

*mg/mL

**mg acid formed 100 hours (from 100 to 500 hours reaction time) at 60°C

ND Not Detected

Table 5
Ethanol Reaction Series

	Acetic Acid			Pentanoic Acid		
	100 hrs	500 hrs	** rate	100 hrs	500 hrs	** rate
No ethanol, no catalyst	ND	2.45	.61	ND	2.95	.74
2% Ethanol, no catalyst	ND	1.55	.39	ND	1.60	.40
2% Ethanol, "Bad" MAK	.22	2.35	.53	.20	2.45	.56
No ethanol, "Bad" MAK	.46	2.85	.60	.52	3.00	.62

*mg/mL

**mg acid formed 100 hours at 60°C

ND not detected

Table 6
Results of Paint Analysis

	Acetic* Acid	Pentanoic* Acid
No inhibitor	133	118
2% Ethanol (based on MAK)	83	72
100 ppm Hydroquinone monobenzyl ether	89	318
100 ppm 2,2'-Bis(4-hydroxyphenyl) butane	74	36
100 ppm 2,4,6-Tris(dimethylaminoethyl) phenol	104	68

*mg/ml after 300 hours at 60° C based on MAK

3. 2,2'-Bis(4-hydroxyphenyl) butane was the best inhibitor tested.

4 CONCLUSIONS AND RECOMMENDATIONS

Analysis of commercial MAK showed the presence of acetic acid, formic acid, 2-ethyl hexanoic acid, pentanoic acid and other trace compounds, which occur when the MAK is synthesized. Reaction of purified MAK indicated that an increase in acid content is caused by an auto-catalytic oxidation reaction, which oxidizes MAK to acetic and pentanoic acids. Such a reaction is reduced, but not eliminated, by using purified MAK. The reaction is also reduced by free-radical and peroxide inhibitors. The best inhibitors were found to be ethanol, 2,2'-Bis(4-hydroxyphenyl) butane, hydroquinone monobenzyl ether, and 2,4,6-tris(dimethylaminoethyl) phenol; however, no inhibitor will eliminate acid formation indefinitely. None of these compounds is deleterious to the paint.

Since it is impossible to eliminate acid formation in MAK completely, acceptance of MAK with the lowest practicable acid number possible would reduce acid formation. The use of the inhibitors listed above, together with low acid number MAK, should reduce acid formation rate to an acceptable level.

Since the oxidation reaction involves alpha hydrogens, a change to a ketone solvent that does not have alpha hydrogens (t-butyl methyl ketone, if possible) would reduce acid formation.

In this study, all reactions were accelerated by elevating the temperature of the reaction. Since this study did not compare the reaction rates at temperatures more typical of those used for storing manu-

factured paints, it is recommended that a testing program be initiated using low acid number MAK and inhibitors in the paint formulation. This would allow comparisons under normal storage conditions.

APPENDIX A: CORPS OF ENGINEERS VINYL FORMULATIONS*

Vinyl-Type White (or Gray) Paint

Table A1
Formula V-766e

Ingredients	Percent by Weight
Vinyl resin, Type 3	5.6
Vinyl resin, Type 4	11.6
Titanium dioxide and (for gray) carbon black	13.0
Diisodecyl phthalate	2.9
Methyl isobutyl ketone	32.0
Toluene	34.7
Orthophosphoric acid	2
	100.0

Table A2
Formula V-766e(AP)

Ingredients	Percent by Weight
Vinyl resin, Type 3	5.4
Vinyl resin, Type 4	11.1
Titanium dioxide and (for gray) carbon black	12.5
Diisodecyl phthalate	2.9
Toluene	11.2
Nitropropane solvent	48.0
Methyl ethyl ketone	8.7
Orthophosphoric acid	0.2
	100.0

*Text taken from *Painting Hydraulic Structures and Appurtenant Works*, Civil Works Construction Guide Specification CW-09940 (Office of the Chief Engineers, August 1981)

Ingredient Materials and Thinners for Special Paint

The following ingredient materials apply only to those paints whose formulations are shown in Tables A1 and A2.

Pigments

Carbon Black. Carbon black shall conform to ASTM D 561, Type I or II.

Titanium Dioxide. The titanium dioxide in vinyl paint Formula V-766c shall be one of the following: Titanox 2160 or 2101, Titanium Pigment Corp.; Ti-Pure 960, E. I. Dupont DeNemours and Co., Inc.; Unitane OR-650, American Cyanamid Co.; Zopaque R-88S, Glidden Pigments.

Resins, Plasticizer

Diisodecyl Phthalate shall have a purity of not less than 99.0 percent, shall contain not more than 0.1 percent water, and shall have an acidity (calculated as acetic acid) of not more than 0.005 percent by weight.

Vinyl Resin, Type 3. Vinyl resin, Type 3, shall be vinyl chloride-acetate copolymer of medium average molecular weight produced by a solution polymerization process and shall contain 85 to 88 percent vinyl chloride and 12 to 15 percent vinyl acetate by weight. The resin shall have film-forming properties and shall, in the specified formulations, produce results equal to "Vinylite" resin VYHH, as manufactured by the Union Carbide Corporation.

Vinyl Resin, Type 4. Vinyl resin, Type 4, shall be a copolymer of the vinyl chloride-acetate type produced by a solution polymerization process; it shall contain (by weight) 1 percent interpolymerized diabasic acid, 84 to 87 percent vinyl chloride, and 12 to 15 percent vinyl acetate. The resin shall have film-forming properties and shall, in the specified formulations, produce results equal to "Vinylite" resin VMCH, as manufactured by the Union Carbide Corporation.

Orthophosphoric Acid shall be a chemically pure 85 percent grade.

Solvents and Thinners

Methyl Ethyl Ketone (MEK) shall conform to the ASTM Designation: D 740.

Methyl Isobutyl Ketone (MIBK) shall conform to ASTM Designation: D 1153.

Methyl Isoamyl Ketone (MIAK) shall be of at least 97 percent purity, shall have a distillation range of 139° to 149°C, and shall have specific gravity (at 20, 20°C) of 0.812 to 0.815. The acidity in 1 gram of the material shall be neutralized by not more than .20 milligrams of potassium hydroxide.

Nitropropane Solvent shall have a distillation range of 119° to 113°C and shall have a maximum acidity of .2 percent (calculated as acetic acid). Nipar S-30, manufactured by Commercial Solvents Corp., has these properties.

Toluene shall conform to ASTM D 362.

Thinner ME-80 shall consist of 80 percent (minimum) methyl ethyl ketone (MEK) and 20 percent toluene by volume.

Thinner NP-10 shall consist of 67 percent nitropropane solvent, 15 percent methyl ethyl ketone, and 18 percent toluene by volume.

APPENDIX B: FORMULA No. 1253

Material	Percent by Weight
Vinyl resin type 4 ¹	12.2
Vinyl resin type 3 ²	6.1
Diisodecyl phthalate	3.1
Titanium dioxide ¹	14.0
MAK	20.6
MPK	32.2
Toluene	11.6
Orthophosphoric acid	0.2
	100.0

¹Union Carbide Vinylite VMCH.

²Union Carbide Vinylite VYHH.

¹Titanium Pigment Corporation Titanox 2062.

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1. Paint. 2. Solvents. 3. Methyl-n-amyl ketone. I. Beitelman, Alfred D. II. Title. III. Series : Technical report (Construction Engineering Research Laboratory) ; M-331.

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